

Aging in a simple model of a structural glass

Luca Peliti^{1,2} and Mauro Sellitto¹

¹ Dipartimento di Scienze Fisiche and Unità INFM,
Università “Federico II”, Mostra d’Oltremare, Pad. 19, I-80125 Napoli, Italy.

² Associato INFM, Sezione di Napoli.

Abstract

We consider a simple model of a structural glass, represented by a lattice gas with kinetic constraints in contact with a particle reservoir. Quench below the glass transition is represented by the jump of the chemical potential above a threshold. After a quench, the density approaches the critical density—where the diffusion coefficient of the particles vanishes—following a power law in time. In this regime, the two-time self-correlation functions exhibit aging. The behavior of the model can be understood in terms of simple mean-field arguments.

1 INTRODUCTION

Although glasses are considered the paradigmatic example of long-lived violation of thermodynamical equilibrium, the detailed nature of this violation is still the subject of much debate [1, 2]. Phenomenologically, a glass is an undercooled liquid, quenched below a temperature such that its viscosity exceeds 10^{13} Poise. In this situation, the glass can be considered “solid” in the sense that its molecules rattle within a “cage” formed by their neighbors and do not leave it, at least within experimental time scales. However, even in the glassy state, the system does not reach a time-independent statistical state, but rather keeps evolving at a slower and slower pace as the time t_w elapsed since its quench increases. This is the origin of the striking aging effects observed in glasses [3, 4]. Aging corresponds to the property that, while one-time quantities like the average energy, volume, etc., appear to be invariant under time translations, two-time correlations and responses exhibit a non trivial dependence on both of their arguments [5]. Similar properties have also been observed in spin-glasses [6, 7] and in fact appear quite frequently, provided one takes the infinite size limit *before* taking the infinite time limit [8]. It now appears that aging can be described by a consistent and robust phenomenology, in which several apparently unrelated properties are brought together. On the one hand, in purely relaxational systems, the lack of time-translation invariance (TTI) in the correlation functions is associated with the violation of the fluctuation-dissipation theorem (FDT) [8]. This violation can be related to entropy production [9] and leads to the definition of an effective frequency-dependent temperature out of equilibrium [10].

Aging properties have been thoroughly investigated within spin-glass models [11] which are closely related to the mode-coupling theories of structural glasses [1, 2]. The spin-glass models proposed as a description of structural glasses lack, however, a transparent physical interpretation in terms of particles and involve a complex, random hamiltonian which is hard to justify as a description of a fluid. Their justification is rather *a posteriori* in the sense that the phenomena they exhibit recall the behavior of structural glasses. On the other hand a class of very simple kinetic models have been introduced to describe the slowing down of the dynamics [12, 13]. These models are defined by kinetic rules involving a selection of the possible configuration changes (“moves”) and are therefore called models with constrained dynamics. The kinetic rules satisfy detailed balance and are compatible with a Boltzmann-Gibbs equilibrium distribution involving a hamiltonian, usually chosen to be a trivial

one. The constraints are alone responsible for the slowing down of the dynamics because, near any allowed configuration, there are only few configurations which satisfy them. Since the hamiltonian is trivial, it is easy to prepare the system in an equilibrium state. By following its subsequent evolution, one can then collect data on the equilibrium correlation functions, which exhibit TTI by definition. In order to observe aging and FDT violation, it is necessary to prepare the sample in an out-of-equilibrium state. One way to achieve this goal is to introduce a conjugate field which plays the role of the temperature, and to simulate the quench by a drastic change of this field.

In the present contribution, we consider a lattice-gas model introduced by Kob and Andersen [14] and generalize it to allow particle exchange with a reservoir [15]. The kinetic constraints prevent the particle from moving when it has too many neighbors: the detailed balance condition is satisfied if the particle cannot move also if it *would have* too many neighbors after the move. As a consequence, the evolution of the system slows down and becomes sluggish when the particle density ρ increases: when $\rho > \rho_c \simeq 0.88$ the self-diffusion constant D vanishes [14].

We have allowed the system to exchange particles with a reservoir, introducing therefore the intensive variable $\mu/k_B T$ (the ratio of the chemical potential to the absolute temperature), conjugate to the total number of particles. Since the hamiltonian is trivial, temperature does not play any significant role and we can set $k_B T = 1$ throughout. The equilibrium equation of state $\rho = \rho_{\text{eq}}(\mu)$ can be then trivially calculated. There is therefore a critical value μ_c of μ defined by $\rho_{\text{eq}}(\mu_c) = \rho_c$. This value plays the role of the glass temperature. In particular a quench is represented by a jump in μ from below to above μ_c , corresponding to a sudden compression.

Remarkably, this simple model exhibits a number of glassy properties so far obtained only in much more complicated models [15]. One can perform numerical experiments analogous to smooth cooling, quench, and hysteresis cycles: namely, one can let μ increase smoothly, perform a cycle, or jump suddenly above μ_c . In the first case the density ρ first increases, then reaches a plateau value that depends on the compression speed: the slower the compression, the higher the value. The critical density ρ_c could apparently be reached in the limit of zero speed. In the second case, the density appears to follow a hysteresis cycle whose area decreases as the compression speed decreases. And finally, in the case of a quench, the density appears to approach the critical one like a power law. In this case, aging effects in the self-correlation function $B(t, t') = \langle |\vec{r}(t) - \vec{r}(t')|^2 \rangle$ are evident. We show here that the power-law relaxation of the density can be interpreted as a consequence of the fact that the diffusion coefficient vanishes at ρ_c , and that this in turns explains the aging effects in $B(t, t')$. A simple mean-field-like theory is proposed, which could act as a guide for further numerical investigations.

Section 2 contains the definition of the model and the results of its simulation. Sec. 3 contains a simple mean-field theory which accounts for the behavior of the model under quench. Sec. 4 contains a brief conclusion and hints for further investigation. Some numerical results reported in Sec. 2 had already been published in ref. [15].

2 NUMERICAL RESULTS

We consider the kinetic lattice-gas model studied by Kob and Andersen (KA) [14]. The system consists of N particles in a cubic lattice of side L , ($V = L^3$) with periodic boundary conditions. There can be at most one particle per site. Apart from this hard core constraint there are no other static interactions among the particles. At each time step a particle and one of its neighbouring sites are chosen at random. The particle moves if the three following conditions are all met:

1. the neighbouring site is empty;
2. the particle has less than m nearest neighbours;
3. the particle will have less than m nearest neighbours after it has moved.

The rule is symmetric in time, detailed balance is satisfied and the allowed configurations have the same weight in equilibrium. Significant results are obtained when the threshold m is set to 4 for a square lattice in three dimensions. With this simple definition one can straightforwardly proceed to study the dynamical properties of the model at equilibrium.

Kob and Andersen [14] have studied this model starting from an equilibrium configuration, which is obtained very simply by filling in turn each site of the lattice with a probability equal to the density ρ . In this way, TTI is satisfied by construction. One observes, in particular, that the diffusion coefficient of the particles vanishes above the critical density $\rho_c \simeq 0.88$, and behaves like $|\rho - \rho_c|^\phi$ for ρ smaller, but close to ρ_c .

In order to study aging effects, we have generalized [15] the KA model by allowing the particles to appear and disappear on a single two dimensional layer (the “surface”). This event takes place with the following Montecarlo rule: a site on the surface is chosen at random; if it is empty we add a particle, otherwise we remove the particle with probability $e^{-\mu}$. We assume $\mu > 0$, since however the interesting behavior takes place at high density ($\rho > 0.5$). Because of the periodic boundary conditions, the sample can also be conceived as a slab, whose upper and lower surfaces (placed, say, at $z = \pm L/2$) are in contact with the reservoir. For each value of μ it is trivial to evaluate the equilibrium density

$$\rho_{\text{eq}}(\mu) = (1 + e^{-\mu})^{-1}. \quad (1)$$

If $\rho_{\text{eq}}(\mu) < \rho_c$, the system rapidly reaches the equilibrium state. There is therefore a critical value, μ_c , of μ , defined by $\rho_{\text{eq}}(\mu_c) = \rho_c$. A quench corresponds to a jump of μ from below to above μ_c . Therefore, μ plays a role analogous to the inverse temperature in mode-coupling theories. We then observe (see fig. 1) that after a quench ρ never exceeds ρ_c , but rather approaches it like a power law in time:

$$\rho(\tau) \propto \tau^{-z}, \quad (2)$$

where τ is the “effective time” after the quench (see later) and the exponent z is approximately equal to 0.3.[16] Let us remark that $z\phi = 1$ within the errors.

The self-correlation function $B(t, t')$ is defined by

$$B(t, t') = \langle |\vec{r}(t) - \vec{r}(t')|^2 \rangle, \quad (3)$$

where $\vec{r}(t)$ and $\vec{r}(t')$ are the positions of the same particles at times t and t' respectively. The average must be defined with some care, since the particles may leave or enter the system. We define it by averaging only over the particles which are present at both times.

From now on we denote the smaller of the two times t, t' by t_w (the “waiting time”). Aging corresponds to the fact that $B(t, t_w)$ does not depend only on $t - t_w$, but rather appears to be a function of t/t_w . Similar results have been obtained for the p -spin spherical spin-glass model [8]. From the figure it is evident that for small values of t_w TTI approximately holds, and aging sets in only for larger values of t_w . In fact, we find here a phenomenon already encountered by Kob and Barrat [17] in Lennard-Jones systems: one has to consider an *effective* waiting time that takes into account the relaxation time of the system before the quench. Hence, one should define an effective waiting time $\tau_w = t_w + \tau_0$, where τ_0 is the relaxation time characteristic of the equilibrium situation [17]. Figure 4 shows that, if one plots $B(t + t_w, t_w)$ vs. t/τ_w , the curves lie roughly on top of one another. The deviations are probably due to finite size effects, e.g., to particles that escape from the sample. Indeed, since the contribution of these particles to $B(t + t_w, t_w)$ has not been included, the mean squared displacement has a tendency to be underestimated at long times. The plot exhibits the waiting-time dependence of the diffusion constant and is consistent with a simple argument suggesting that diffusion is logarithmic in the presence of aging [18].

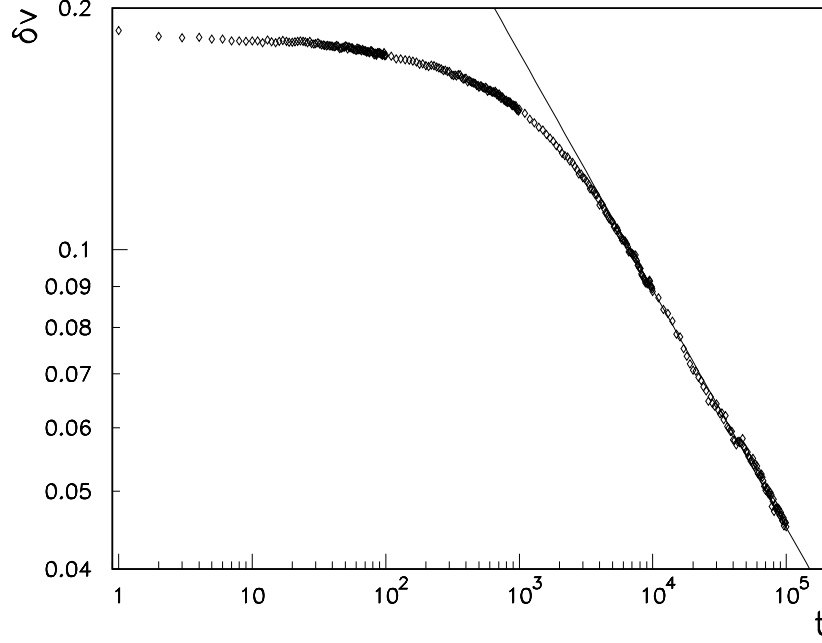


Figure 1: Relaxation of the excess specific volume $\delta v = v - v_\infty$, where $v = 1/\rho$, $v_\infty = 1/\rho_c$, after a quench to the subcritical value $1/\mu = 1/2.2$. The density of initial configuration is 0.75. The straight line is $\delta v = 1.36 \cdot t^{-0.296}$, with $v_\infty = 0.88$.

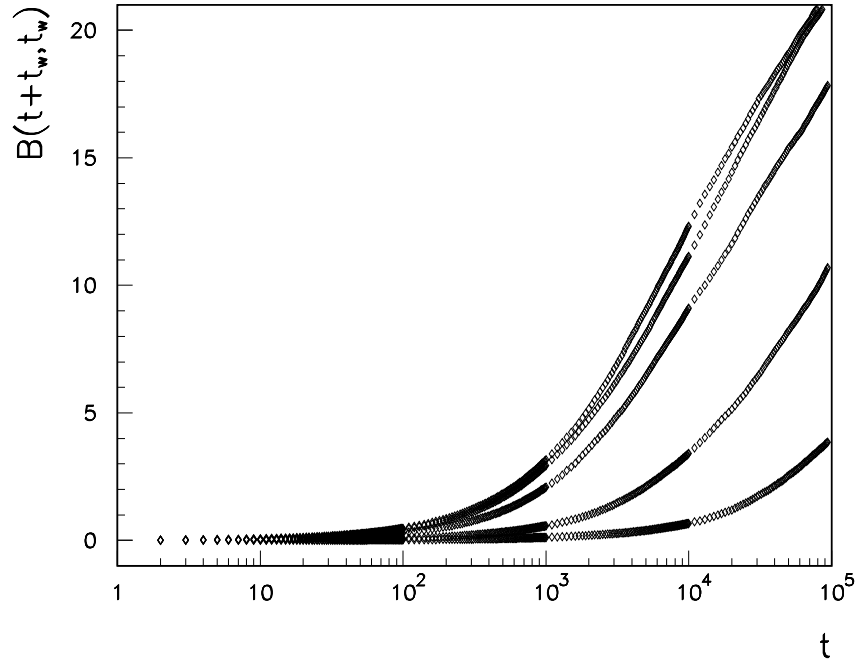


Figure 2: Mean square displacement vs. time after a quench to the value $1/\mu = 1/2.2$. The waiting times are $t_w = 10, 10^2, 10^3, 10^4, 10^5$. The density of initial configuration is 0.75. Average over ten samples.

3 MEAN-FIELD ARGUMENTS

In this section we show how we can understand the results reported above by simple mean-field-like arguments. Let us assume, as found by KA, that $D(\rho) \sim (\rho_c - \rho)^\phi$, where, as found by KA, $\phi \simeq 3.1$. We consider the sample as a slab, whose free surfaces at $z = \pm L/2$ are in contact with the reservoir and therefore rapidly reach a density equal to the critical one. Within the sample, the density $\rho(z, t)$ satisfies the following non-linear diffusion equation:

$$\frac{\partial \rho}{\partial t} = \frac{\partial}{\partial z} \left[D(\rho(z, t)) \frac{\partial \rho}{\partial z} \right], \quad (4)$$

with the boundary conditions $\rho(L/2) = \rho(-L/2) = \rho_c$, and where $\rho(z, t) < \rho_c$ for $-L/2 < z < L/2$ and all t . Changing variable $y = \rho - \rho_c$ we obtain the equation

$$\frac{\partial y}{\partial t} = \phi y^{\phi-1} \left(\frac{\partial y}{\partial z} \right)^2 + y^\phi \frac{\partial^2 y}{\partial z^2}. \quad (5)$$

One can look for solutions of the form $y(z, t) = Y(t)f(z)$. One obtains

$$Y(t) \sim t^{-1/\phi}, \quad (6)$$

corresponding to a power-law relaxation of the density with an exponent $z = 1/\phi$, and a differential equation for the density profile $f(z)$:

$$f(z) = \frac{\partial}{\partial z} \left[f^\phi(z) f'(z) \right], \quad (7)$$

with the boundary conditions

$$f(\pm L/2) = 0. \quad (8)$$

It is easy to see that this equation allows for solutions of the form

$$f(z) = f_0 \hat{f}(z/L), \quad (9)$$

where

$$f_0 \propto L^{2/(1-\phi)}, \quad (10)$$

and where the universal profile $\hat{f}(x)$ satisfies

$$\hat{f}(x) = \phi \hat{f}^{\phi-1}(\hat{f}')^2 + \hat{f}^\phi \hat{f}'', \quad (11)$$

where one can choose the boundary conditions $\hat{f}(0) = f(0)/f_0 = 1$, $\hat{f}'(0) = 0$. The result of a numerical integration of this equation with the KA value of $\phi = 3.1$ is shown in fig. 3. The solution vanishes for $x = x_0 \simeq 0.72$. The full solution is therefore $f(z) = f(0)\hat{f}(2x_0 z/L)$. Unfortunately our simulation data are still too noisy to allow for a meaningful comparison with this prediction.

Let us now consider the effects of a varying diffusion constant on the self-correlation function $B(t, t_w)$. In a simple minded approach we would obtain

$$B(t, t_w) = \int_{t_w}^t dt' D(t'). \quad (12)$$

If we assume $D(t) \propto t^{-\zeta}$ we obtain

$$B(t, t_w) \propto (t^{1-\zeta} - t_w^{1-\zeta}). \quad (13)$$

However, in our case, we have $\zeta = z\phi = 1$, and a simple integration leads to

$$B(t, t_w) \propto (\log t - \log t_w). \quad (14)$$

This is the functional obtained in ref. [18] from the hypothesis that $B(t, t_w)$ depends only on t/t_w and from the “triangle relation” for $B(t, t')$:

$$B(t, t') = B(t, s) + B(s, t'), \quad \text{for } t' < s < t, \quad (15)$$

which stems out of the statistical independence of particle displacements over nonoverlapping time intervals. This functional form is borne out by the simulations, as can be seen by fig. 4.

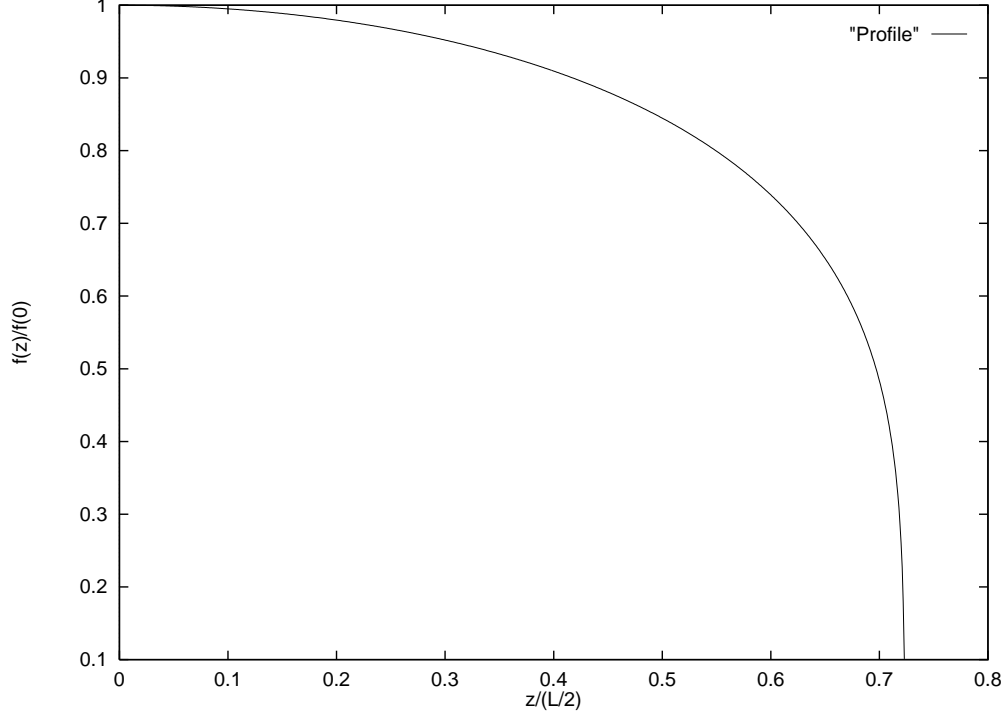


Figure 3: Universal density profile $f(z)/f(0)$ vs. $z/(L/2)$. We have chosen the KA value of $\phi = 3.1$.

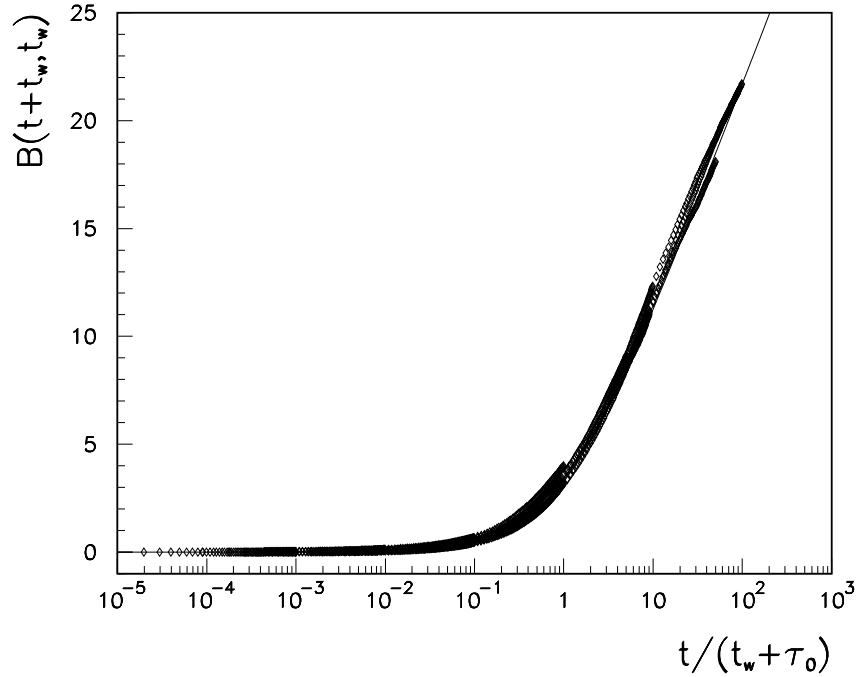


Figure 4: Mean squared displacement $B(t + t_w, t_w)$ vs. scaled time t/τ_w (where $\tau_w = t_w + \tau_0$) for $t_w = 10, 10^2, 10^3, 10^4, 10^5$, and $\tau_0 = 10^3$. Quench to the subcritical value $1/\mu = 1/2.2$, starting from density 0.75. The full line corresponds to $B(t + t_w, t_w) \propto (\log(t + t_w) - \log t_w)$. System of size 20^3 , average over ten samples.

4 DISCUSSION

We find remarkable that this toy model—based as it is upon indefensible assumptions—exhibits a behavior so similar to those of much more complex models. Perhaps the most appealing aspect is the fact that aging appears as a consequence of the slow (power-law) approach to the critical density. This approach bears some similarity to self-organized criticality: after a sudden compression, the system endeavors to accommodate as many particles as it can: but, if the critical density is exceeded, particle diffusion stops and no more particles can get in. The result is an ever slower approach to the critical density, and it may be said that the system ages because it approaches criticality. Similar considerations in the context of the Bak-Sneppen model have been made by Boettcher and Paczuski [19]. In our case they can be made explicit and quantitative, even within a mean-field-like approach.

Several interesting informations concerning the breakdown of thermodynamical equilibrium can be obtained from response functions. In our case, one can consider applying a small constant force \vec{F}_α to particle α between times t_w and t . As a consequence, the particle suffers an extra displacement $\delta\vec{r}_\alpha(t, t_w)$. The response function $\chi(t, t_w)$ is then defined as [20]

$$\chi(t, t_w) = \frac{\partial \langle \delta r_i(t, t_w) \rangle}{\partial F_i}, \quad (16)$$

where i is one of the coordinates. The celebrated CK plot [8] of the response function vs. the correlation function should then appear as a broken line, where the break takes place in correspondence of the value of $B(t, t_w)$ for which TTI no longer holds. If the “mean-field” arguments given above hold, the response of the aging system should be locked in at what it would exhibit at the critical density. The slope of the FDT violating line should then be independent of the quench value of μ . It would be nice to be able to put this slope in relation with “universal” properties of the model, like ϕ , but we have so far been unable to obtain this relation.

Acknowledgements

It is strange to think that it will not be possible to discuss this model with Giovannino. We think that he would have liked it, because it has one of the qualities he appreciated most: coming close to the heart of a physical problem in simple ways. We owe much to discussions with Giovannino, and to his playful and serious ways of making physics. LP would like to apply to Giovannino and himself the old hebrew saying, in the words of Lorenzo Da Ponte: *E da' discepoli imparai più che da tutti*.

Both authors warmly thank Jorge Kurchan for having initiated this work and for his continual interest in it. This work has been done while LP was visiting the Laboratoire de Physico-Chimie Théorique of the Ecole Supérieure de Physique et Chimie Industrielles de la Ville de Paris, supported by a Chaire Joliot. Part of the work by MS was done during a visit to the same laboratory. Both authors thank the Laboratoire and its Director, A. Ajdari, for hospitality and for support. MS also thanks Th.M. Nieuwenhuizen for support and hospitality at the Van der Waals-Zeeman Laboratorium.

References

- [1] Götze W., “Aspects of structural glass transitions”, in: *Liquids, freezing and the glass transition*, Les Houches 1989, J.-P. Hansen, D. Levesque and J. Zinn-Justin Eds. (North-Holland, Amsterdam, 1991) p. 289.
- [2] Götze W. and Sjögren L., Rep. Prog. Phys. 55 (1992) 241.
- [3] Hodge, I., J. Non Cryst. Solids (1994) 211; Science 267 (1996) 1945.

- [4] Struik L.C.E., *Physical Aging in Amorphous Polymers and Other Materials* (Elsevier, Houston, 1978).
- [5] For a recent review, see: Vincent E., Hammann J., Ocio M., Bouchaud J.-P. and Cugliandolo L. F., Slow dynamics and aging in spin glasses, in *Complex behavior of glassy systems*, Sitges 1996, E. Rubí Ed., cond-mat/9607224.
- [6] Lundgren L., Svedlindh P., Nordblad P. and Beckman O., Phys. Rev. Lett. 51 (1983) 911.
- [7] Vincent E., Hammann J. and Ocio M. in *Recent Progress in Random Magnets*, D.H. Ryan Ed. (World Scientific, Singapore, 1992) p. 207.
- [8] Cugliandolo L.F. and Kurchan J., Phys. Rev. Lett. 71 (1993) 173; Phil. Magaz. B71 (1995) 50.
- [9] Cugliandolo L.F., Dean D.S. and Kurchan J., Phys. Rev. Lett. 79 (1997) 2168.
- [10] Cugliandolo L.F., Kurchan J. and Peliti L., Phys. Rev. E55 (1997) 3898.
- [11] For a recent review, see: Bouchaud J.-P., Cugliandolo L.F., Kurchan J. and Mézard M., Out of equilibrium dynamics in spin glasses and other glassy systems, in *Spin glasses and random fields*, A.P. Young, Ed. (World Sci., Singapore, 1997) cond-mat/9702070.
- [12] Fredrickson G.H. and Andersen H.C., Phys. Rev. Lett. 53 (1984) 1244; J. Chem. Phys. 83 (1985) 5822.
- [13] Fredrickson G.H. and Brawer S.A., J. Chem. Phys. 84 (1985) 3351.
- [14] Kob W. and Andersen H.C., Phys. Rev. E48 (1993) 4364.
- [15] Kurchan J., Peliti L. and Sellitto M., Europhys. Lett. 39 (1997) 365.
- [16] The data presented here are the result of more careful simulations than those quoted in ref. [15]. In particular, the quench is more “gentle” (starts from a value of μ closer to μ_c), what allows the asymptotic power law behavior to set in more rapidly. With these simulations, the small discrepancy between the values of ρ_c with ref. [14] has disappeared.
- [17] Kob W. and Barrat J.-L., Phys. Rev. Lett. 78 (1997) 4581.
- [18] Parisi G., Phys. Rev. Lett. 79 (1997) 3660.
- [19] Boettcher, S., and Paczuski, M., Phys. Rev. Lett. 79 (1997) 889.
- [20] L. Cugliandolo and P. Le Doussal, Phys. Rev. E53 (1996) 1525.